

PB92-119015

Estimating Critical Loads of Sulfate to Surface Waters in the  
Northeastern United States: A Comparative Assessment of Three  
Procedures for Estimating Critical Loads of Sulfate for Lakes

ManTech Environmental Technology, Inc., Corvallis, OR

Prepared for:

Corvallis Environmental Research Lab., OR

Nov 91



EPA600/3-91/062

November 1991

PE92-1190 15

**ESTIMATING CRITICAL LOADS OF SULFATE TO SURFACE WATERS IN  
THE NORTHEASTERN UNITED STATES:  
A Comparative Assessment of Three Procedures for Estimating Critical Loads of  
Sulfate for Lakes**

Paul W. Shaffer, Barbara Rosenbaum, George R. Holdren, Jr.  
Timothy C. Strickland, and Michael K. McDowell  
ManTech Environmental Technology  
US EPA Environmental Research Laboratory  
200 SW 35th Street, Corvallis, Oregon 97333 USA

Paul L. Ringold  
U.S. Environmental Protection Agency,  
Office of Research and Development, Washington, D.C. 20460 USA

Robert S. Turner  
Oak Ridge National Laboratory\*, Oak Ridge, Tennessee 37831 USA

Patrick F. Ryan  
Science Applications International Corporation, Oak Ridge, Tennessee 37831 USA

David Bernard  
ESSA Ltd., Box 12155 (808 Nelson Street)  
Vancouver, B.C. V6Z 2H2, Canada

\* managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract # DE-AC05-84OR21400.

**ENVIRONMENTAL RESEARCH LABORATORY-CORVALLIS  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
CORVALLIS, OR 97333**

| TECHNICAL REPORT DATA<br>(Please read instructions on the reverse before completing)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                  |                                                                                                                                                                                     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. REPORT NO.<br>EPA/600/3-91/062                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 2.                                               | 3. PB92-119015                                                                                                                                                                      |
| 4. TITLE AND SUBTITLE<br>Estimating Critical Loads of Sulfate to Surface Waters in the Northeastern United States                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 5. REPORT DATE<br>11/26/91                       | 6. PERFORMING ORGANIZATION CODE<br>EPA/ORD                                                                                                                                          |
| 7. AUTHOR(S)<br>P. W. Shaffer, B. Rosenbaum, G. R. Holdren, Jr.<br>T. C. Strickland, M. K. McDowell, P. L. Ringold,<br>D. S. Turner, P. F. Ryan, and D. Bernard                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 8. PERFORMING ORGANIZATION REPORT NO.            | 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>1st 5, ManTech Technology Services, ERL-<br>Corvallis; Ringold, US EPA, Wash. DC;<br>Turner, ORNL; Ryan, SAIC; Bernard, ESSA, CANADA |
| 10. PROGRAM ELEMENT NO.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 11. CONTRACT/GRANT NO.                           | 12. SPONSORING AGENCY NAME AND ADDRESS<br>US Environmental Protection Agency<br>Environmental Research Laboratory<br>200 SW 35th Street<br>Corvallis, OR 97333                      |
| 13. TYPE OF REPORT AND PERIOD COVERED<br>Published Report                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 14. SPONSORING AGENCY CODE<br>EPA/600/O2         | 15. SUPPLEMENTARY NOTES<br>1991: U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR                                                             |
| 16. ABSTRACT<br>It is important to note that no attempt to evaluate or identify any of the results presented here as right/wrong, or to rank the reliability of results was made. The objective, rather, has been to generate sets of critical load estimates using multiple models and data sets, and to compare the results. The results presented here represent a first step in the critical evaluation of models used to estimate critical loads and to cross-validate model-based estimates. The results have demonstrated substantial variability in critical loads estimated using different datasets and procedures. Given these results, it seems clear that extensive review, refinement, and verification of models and datasets will be required before any critical load estimates can be reliably used. ← |                                                  |                                                                                                                                                                                     |
| 17. KEY WORDS AND DOCUMENT ANALYSIS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                  |                                                                                                                                                                                     |
| a. DESCRIPTORS<br>critical loads, sulfate standard, acidification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | b. IDENTIFIERS/OPEN ENDED TERMS                  | c. COSATI Field/Group                                                                                                                                                               |
| REPRODUCED BY<br>U.S. DEPARTMENT OF COMMERCE<br>NATIONAL TECHNICAL<br>INFORMATION SERVICE<br>SPRINGFIELD, VA 22161                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                  |                                                                                                                                                                                     |
| 18. DISTRIBUTION STATEMENT<br>Release to Public                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 19. SECURITY CLASS (This Report)<br>Unclassified | 20. NO. OF PAGES<br>43                                                                                                                                                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 21. SECURITY CLASS (This page)<br>Unclassified   | 22. PRICE                                                                                                                                                                           |

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## EXECUTIVE SUMMARY

This report was completed as a component of the United States' participation as a signatory to the NO<sub>x</sub> Protocol of the United Nations Economic Community for Europe's Long Range Transboundary Air Pollution (ECE-LRTAP) Convention. It presents an intercomparison of critical loading approaches for one pollutant-receptor pair. The critical loads approach is being developed for consideration in international air pollution management, under the LRTAP Convention and requires the development of information on tradeoffs between ecosystem status and pollution levels. Such information, along with information on the costs of control, is used to set politically acceptable emissions values for pollutants. These values, termed target loads, thus reflect not only ecosystem impact, but economic costs. The purpose of this analysis is not to select the correct method, but rather to determine the significance of different assumptions in implementing the ECE approach.

A variety of ecosystem components are potentially susceptible to adverse impacts from atmospheric sulfate deposition. A comprehensive analysis of critical loads should thus eventually assess all susceptible receptors and indicators, and define the critical load based on the most sensitive receptors and indicators. For this demonstration study, sulfate in surface water was selected as the pollutant-receptor pair for the current examination because the information necessary to evaluate the assumptions are better developed for this pair than for any other candidates (e.g., nitrate effect on soil acidification) in the U.S. Acid neutralizing capacity (ANC) was selected as the indicator, with two values of ANC used as endpoints (0 and 25  $\mu\text{eq/L}$ ). In surface waters dominated by bicarbonate buffer systems, these ANC values roughly correspond to pH values of 5.3 and 6.0, respectively, and have been identified as ecologically significant levels for surface water fauna. The lake chemistry data used in this analysis were generated by the U.S. EPA's Eastern Lake Survey.

Different approaches often result in similar spatial patterns of relatively high and low critical loads, which are roughly comparable to patterns of high and low surface water ANC, but for any given lake system the three estimates generate significantly different critical load estimates. These differences highlight the uncertainties in estimating critical loads for surface waters, and reflect uncertainties in the information and procedures required to make

those estimates. Specific combinations of data aggregation approaches, model usage, sample sets, and endpoints were created which suggested that 45% of northeastern lakes larger than 4 ha may become acidic if sulfate deposition remains as high as 20 kg/ha/yr. However, the magnitude of this estimate is quite dependant upon the prediction method employed; other combinations place the number at 1% for the same deposition level.

The report indicates that variations in predictions arise from multiple sources including: 1) size of sample population, 2) individual model formulations, and 3) method of data aggregation and reporting framework (i.e., regionalization scheme). The results presented here represent a first step in the critical evaluation of models used to estimate critical loads and to cross-validate model-based estimates. Results demonstrated substantial variability in critical loads estimated using different datasets and procedures.

## 1.0 INTRODUCTION

The critical loads approach is being developed for consideration in international air pollution management, under the Long Range Transboundary Air Pollution (LRTAP) Convention. This approach requires the development of information on tradeoffs between ecosystem status and pollution levels, and uses this information, along with information on the costs of control, to set politically acceptable emissions values for pollutants. These value, termed target loads, thus reflect not only ecosystem impact, but economic costs. Formal definitions of these key terms are provided in section 2.0.

In 1988 the United States agreed to sign the United Nations Economic Community for Europe (UN-ECE) NO<sub>x</sub> Protocol and to endorse the establishment of a UN-ECE Work Group on Abatement Strategies. A key feature of these agreements was participation in evaluating the critical loads approach to managing air pollution. In addition, The Clean Air Act Amendments of 1990 request EPA to report on the feasibility of an acid deposition standard.

→ The objective of the U.S. critical loads program has been to develop a framework for estimating critical loads and to evaluate the effects of multiple assumptions inherent in those estimates. A general framework for developing critical loads estimates was developed by the UN-ECE (1990). A flow chart describing this procedure, ~~is provided in Figure 1.~~<sup>8</sup> This status report presents examples of efforts to estimate critical loads of sulfate for surface waters in the United States and discusses the effects of different assumptions on the final estimates. Sulfate in surface water was selected as the pollutant-receptor pair for the current examination because the information necessary to evaluate the assumptions are better developed for this pair than for any other candidates (e.g., nitrate effect on soil acidification) in the U.S. → can't on BDS

The report is organized according to the steps in the framework; it explains the decisions made in each of the steps and identifies the information available to estimate uncertainty and the effects of alternative assumptions. In presenting estimates of critical loads, it must be emphasized that these are preliminary results and estimates. They reflect an effort to demonstrate, and to compare the results of, the implementation of methods as developed in the UN-ECE manual (UN-ECE, 1990). At this time, the U.S. has not adopted a policy on critical loads estimation, and none of the maps are posited as representing correct critical loads. **These maps are not being considered for use in the formulation of policy regarding sulfur emissions.**

# U.S. Critical Loads Program

## Component Aspects of Process Examined

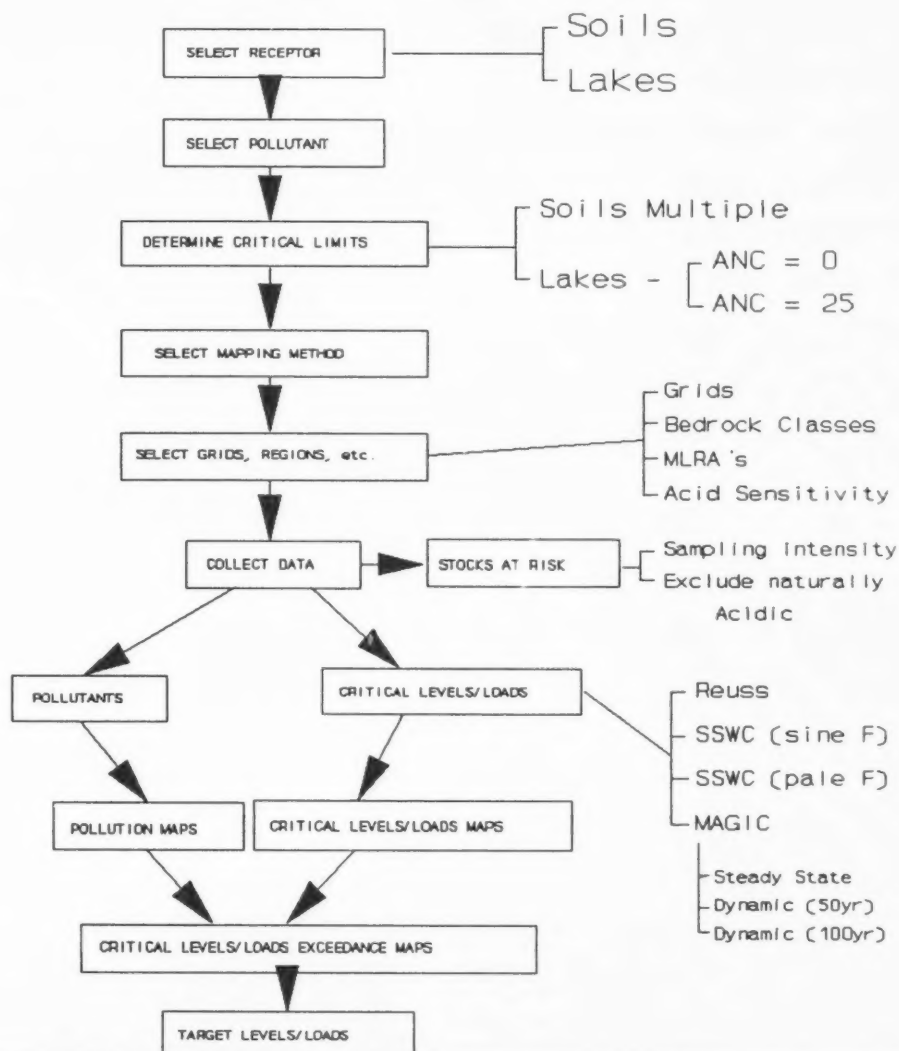


Figure 1. Critical loads development framework.

## **2.0 DEFINITIONS**

The 1991 Report of the Task Force on Mapping (fourth draft) has summarized definitions of critical loads and levels as follows: "The critical loads approach is a procedure for developing optimized abatement strategies by which differentiated emission reductions are arrived at on the basis of scientifically derived critical values. Critical levels means the concentration of pollutants in the atmosphere above which direct effects on receptors, such as plants, ecosystems, or materials, may occur, according to present knowledge. Critical loads is a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge. Target levels and loads are nationally set values, taking into account not only the environmental sensitivity, but also technical, social, economic, and political considerations by individual countries. Target loads/levels may be at, above, or below critical loads/levels.

## **3.0 APPROACH**

The ECE approach (presented in Figure 1) prescribes a series of steps, but does not specify that the steps must be executed in any specific manner. This generic framework provides the flexibility for nations and analysts to adapt it to their peculiar data availability and/or geographic characteristics. The purpose of this analysis is not to select the correct method, but rather to determine the significance of different assumptions in implementing the ECE approach.

### **3.1 Study Region**

Based on several considerations, the northeastern United States was selected as the study region for this demonstration project. The northeastern U.S. contains a large population of lake systems that are potentially sensitive to acidification, but which have diverse watershed, vegetation, and soil characteristics (National Surface Water Survey [NSWS]; Linthurst et al., 1986). These systems have been exposed to a persistent regional gradient of acidic sulfur deposition (Figure 2), and exhibit a range of surface water chemistries in terms of acid-base status (Figure 3). In addition, the region is very "data rich" in that there are extensive data bases characterizing surface water chemistry, sulfate deposition, soil chemistry, etc. There have also been extensive modelling analyses of pollutant transport and deposition, and resulting effects on surface waters in the region

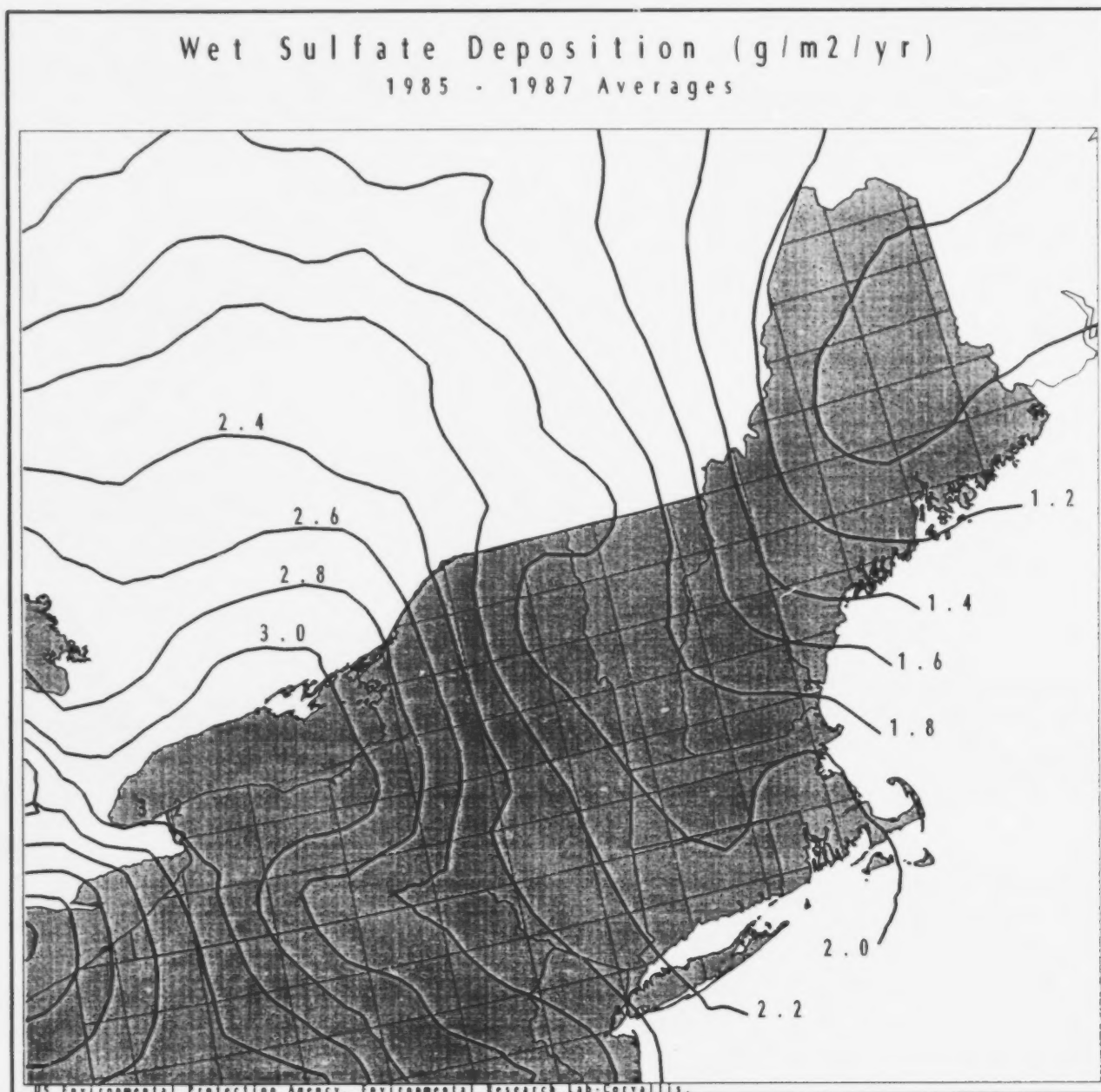
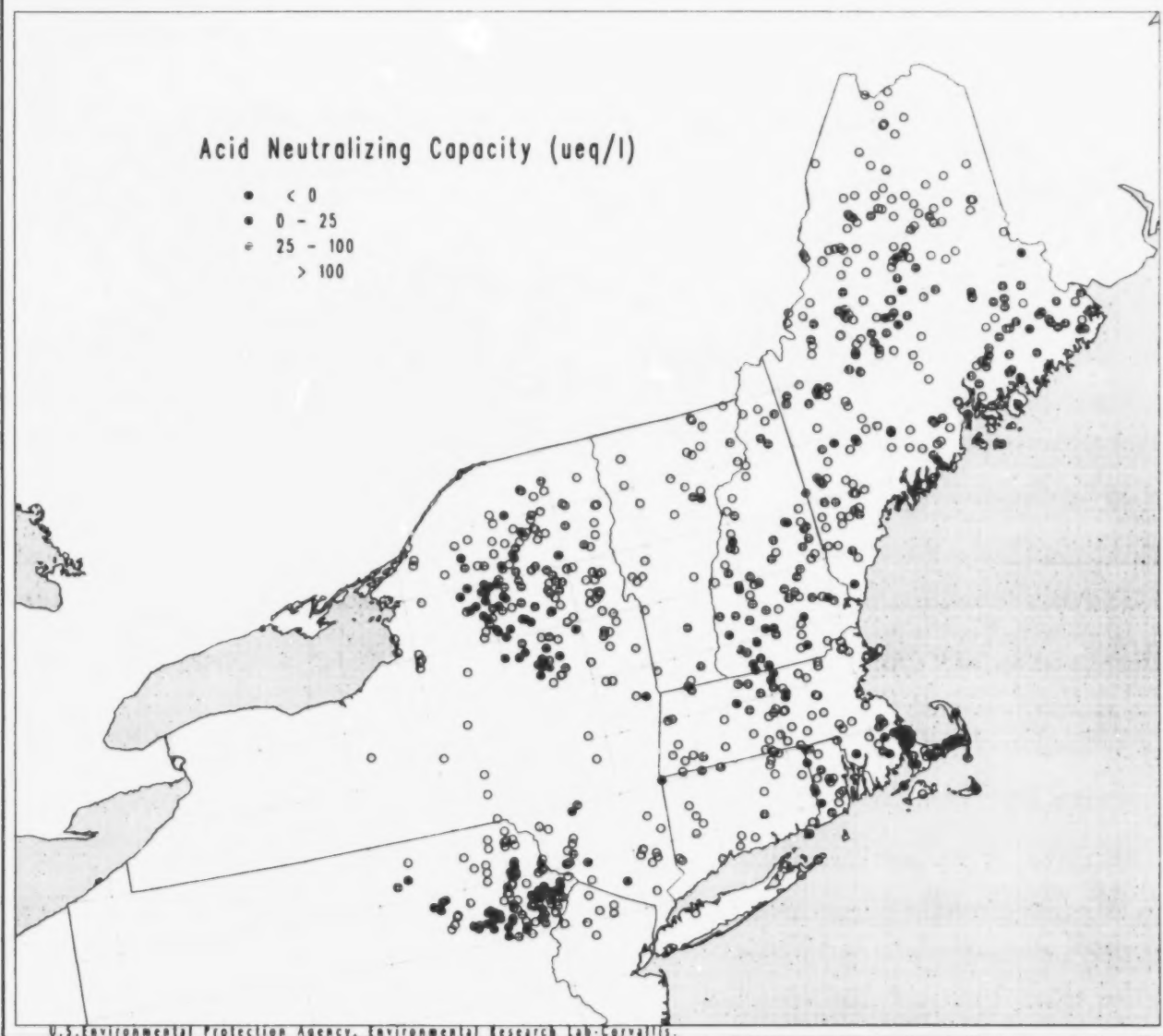


Figure 2. Deposition of wet sulfate in the northeastern United States

## Current Status of NSW5 - ANC



U.S. Environmental Protection Agency, Environmental Research Lab-Corvallis.

Figure 3. Acid neutralizing capacity of lakes in the northeastern United States

(current and altered levels of acidic deposition). Consideration in this report will be limited to a comparative assessment of critical load estimates for deposition of sulfate to lakes in the region, using several approaches for estimation.

### **3.2 Selection of Receptor, Indicator and Endpoints**

A variety of ecosystem components are potentially susceptible to adverse impacts from atmospheric sulfate deposition; a comprehensive analysis of critical loads should eventually assess all susceptible receptors and indicators, and define the critical load based on the most sensitive receptors and indicators. For this demonstration study, surface waters were chosen as the receptor, and acid neutralizing capacity (ANC) as an indicator, with two values of ANC used as endpoints. The choice of surface waters was based on several considerations, including: (1) changes in surface water chemistry have ecological significance, as they are closely related to effects on aquatic fauna, including fish; (2) the relationship between acidic sulfate deposition and surface water acidification is relatively straightforward (e.g., in comparison to effects of nitrogen deposition), and is described by a variety of models, including those selected for use by the Task Force on Mapping (UN-ECE, 1990); and (3) data and a variety of models are available for analyses to estimate sulfate critical loads for surface waters. Calculation of critical loads for surface waters is based on established relationships among deposition, soils, and surface waters, and effects are direct and unambiguous. In contrast, the effects of sulfate and of other airborne pollutants (singly, or in combination) on receptors such as vegetation are, at present, poorly differentiated, leading to major difficulties in the selection of biologically-relevant indicators useful in defining critical loads/levels.

Two approaches can be used to define critical loads for an ecosystem and receptor. One approach is to define a receptor and reference values for a specific indicator (e.g., surface water pH or ANC under current conditions or under inferred historic conditions), and then relate changes in that value to changes in deposition. Under this approach, a critical load would be defined as a deposition loading that resulted in significant adverse changes relative to the reference value. A second, more straightforward procedure has been adopted in this analysis, to define an absolute, or "protective" standard, based on evidence that it represents a threshold value (e.g., pH 6.0) below which adverse ecological effects are likely to occur. The critical load in this instance is the level

of deposition necessary to keep (or in the case of acidic systems, to return) the indicator of concern (pH in the above example) at a value above the threshold value.

For this demonstration study, critical loads are estimated for two endpoint values of ANC -- 0 and 25  $\mu\text{eq/L}$ . In surface waters dominated by bicarbonate buffer systems, these ANC values roughly correspond to pH values of 5.3 and 6.0, respectively, identified as ecologically significant levels for surface water fauna (Nilson, 1986; Baker et al., 1991). In addition, the  $\text{ANC} = 0$  value has been widely used to define acidic surface waters, and provides a useful reference chemistry value. It is important to recognize that the critical loads estimates described in this report, and the ANC values on which they are based, pertain to chronic average values of ANC, and do not consider possible episodic acidification of surface waters.

### 3.3 Calculation of Critical Loads

Three sets of estimates of critical loads for sulfate in surface waters were generated in this demonstration project, using both Level I (single process) and Level II (dynamic process) approaches. Two of these sets rely on the Steady State Water Chemistry (SSWC) Model, described in Section 4.2.2 the ECE draft Mapping Manual (UN-ECE, 1990) and are summarized here. Using sea-salt corrected concentrations of major ions in deposition and in lake water, this procedure first estimates the pre-acidification concentration of base cations as:

$$[\text{BC}]_0^* = [\text{BC}]_t^* - F * ([\text{SO}_4]_t^* - [\text{SO}_4]_0^*) \quad [\text{Eq. 1}]$$

where  $[\text{BC}]^*$  and  $[\text{SO}_4]^*$  are sea-salt corrected concentrations of base cations and sulfate, respectively. Subscripts denote time as the present (t) or pre-acidification (0), and F is Henriksen's F-factor (Henriksen, 1984). Using  $[\text{BC}]_0^*$  estimates from [Eq. 1], the critical load for sulfate is then estimated as:

$$\text{CL}_s = Q * ([\text{BC}]_0^* - [\text{ANC}]_{\text{limit}}) - \text{BC}_d^* \quad [\text{Eq. 2}]$$

where Q is runoff,  $[\text{ANC}]_{\text{limit}}$  is the critical ANC level, and  $\text{BC}_d^*$  is the sea-salt corrected annual average flux of base cations in wet and dry deposition. Critical loads were estimated using

$[\text{ANC}]_{\text{limit}} = 0 \text{ and } 25 \mu\text{eq/L}.$

Two sets of estimates of sulfate critical loads were derived using these equations, differing only by the procedures used to compute estimates of  $F$ . The first set used a relationship described by Brakke et al. (1990) and identified in the UN-ECE draft Mapping Manual:

$$\text{if } [\text{BC}]_t^* < 400 \mu\text{eq/L}, \quad F = \sin(90 * ([\text{BC}]_t^*/S)) \quad [\text{Eq. 3}]$$

$$\text{or if } [\text{BC}]_t^* \geq 400 \mu\text{eq/L} \quad F = 1.00 \quad [\text{Eq. 4}]$$

where  $S$  is an empirically derived value, estimated from data for Norway to be approximately 400  $\mu\text{eq/L}$ , and set equal to 400  $\mu\text{eq/L}$  for this exercise. Values of  $F$  and critical loads developed from equation 3 are hereafter identified as being based on the "Brakke- $F$ ".

The second set of critical load estimates is based on an alternate set of values of  $F$ , which are derived from results of paleoecological (paleo) analysis of diatom remains (and other physical, chemical, and biological markers) from sediment cores of 35 lakes in the Adirondack Mountains of New York (Charles et al., 1990; Whitehead et al., 1990). Paleo data were used to reconstruct the historic changes in lake chemistry, including pH and ANC, from which  $F$  was empirically estimated by Sullivan et al. (1990) as:

$$\text{if } \text{ANC} < 100, \quad F = 0.8731 + (0.004613 * [\text{ANC}]_t) \quad [\text{Eq. 5}]$$

$$\text{or if } \text{ANC} \geq 100, \quad F = 1.33 \quad [\text{Eq. 6}]$$

Values of  $F$  derived from this approach, and associated values of critical loads, are hereafter identified as being based upon "Paleo- $F$ " values.

Consistent with recommendations in the UN-ECE draft Mapping Manual, the third set of critical load estimates was developed using the MAGIC dynamic watershed chemistry model (Cosby et al., 1985a; 1985b), with critical loads estimates developed for a set of northeastern watersheds previously characterized, and for which the MAGIC model had been calibrated, as part of the Direct/Delayed Response Project (DDRP) (Figure 4) (data sources and calibration procedures for MAGIC for these watersheds are described in detail by Church et al., 1989). Model simulations

## Location of Sampled Lakes

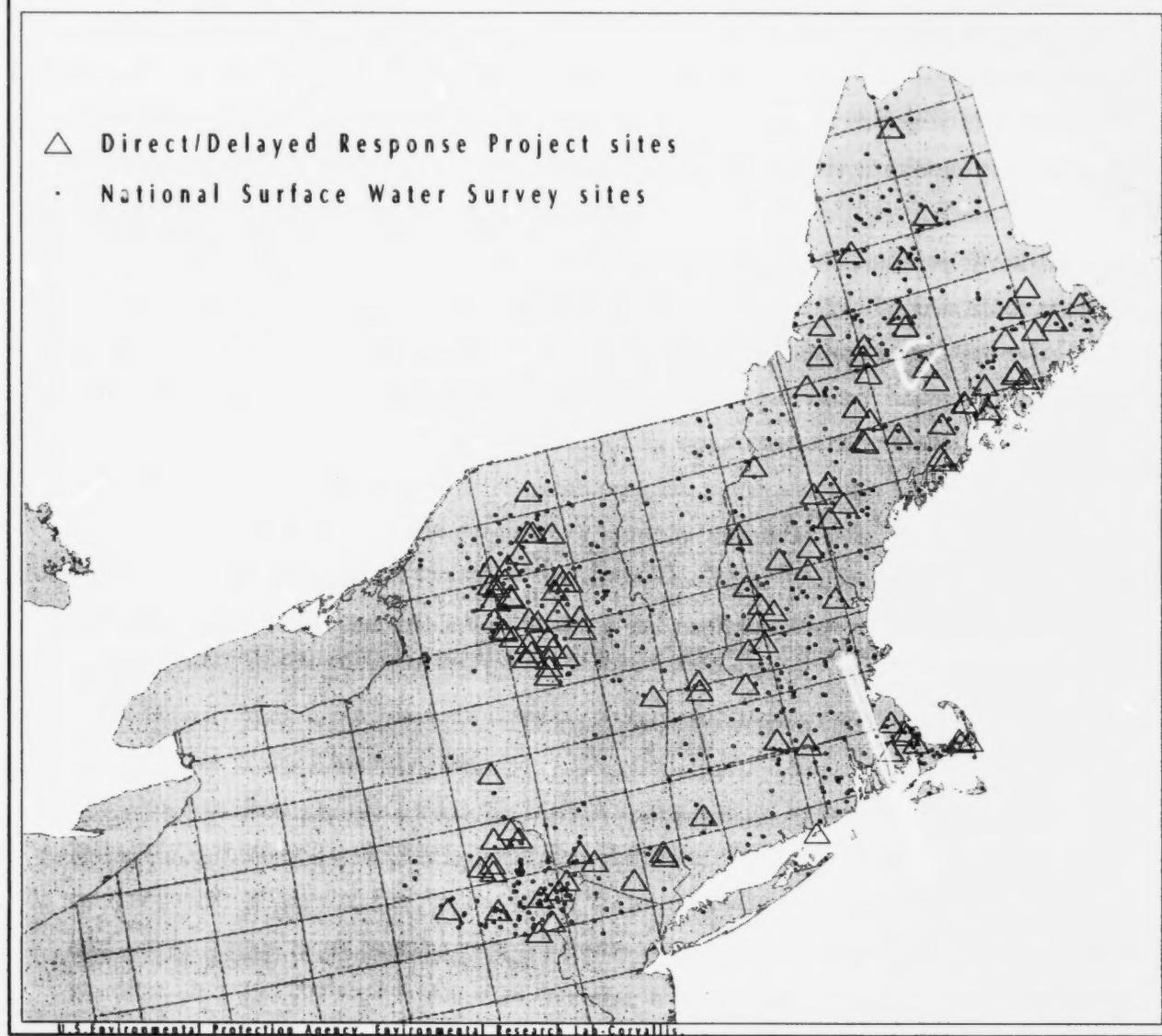


Figure 4. Location maps of ELS lakes in the northeastern United States used for Steady State Water Chemistry analyses and DDRP watersheds used for MAGIC simulations.

were run for a period of 50 years, using six deposition scenarios for each watershed. In the various prediction scenarios, sulfate deposition was held constant from year 1-5, then ramped linearly between years 6-15 to a level 50, 70, 80, 100, 120, or 130 percent of current deposition, then held at the year 15 loading rate from years 16 to 50. For each watershed, projected ANC values at year 50 for the six deposition scenarios were plotted against sulfate deposition in year 50. A regression equation was then fitted to the six points and used to estimate the sulfate loading that would yield an ANC of 0 and 25  $\mu\text{eq/L}$ . In many cases it was necessary to extrapolate to sulfate loadings many times higher than current deposition; the uncertainty in such values is obviously high, but in any case these values indicate critical loads of sulfate that are higher than levels of deposition that might reasonably be expected to occur on these watersheds.

The 50 year period used for MAGIC simulations was sufficient for sulfate to effectively reach steady state on all watersheds (i.e.,  $\text{SO}_4$  output equals  $\text{SO}_4$  input  $\pm 5\%$ ). Because cation exchange continues to act as a net source of base cations throughout the simulation period, however, the 50 year MAGIC estimates of critical loads are higher than those which would be estimated if simulations were run until steady state was attained for cations and ANC. Given the slow rate of change in ANC after year 50 in MAGIC simulations and the uncertainties and assumptions (e.g., no long-term changes in nitrogen dynamics) inherent in long-term simulations, we believe that critical load estimates based on 50 year simulations are useful for comparative analyses, and in any case have a time frame compatible with planning and implementation of sulfur emission control strategies.

### 3.4 Surface Water Chemistry Data

The lake chemistry data used in this analysis were generated by the U.S. EPA's Eastern Lake Survey (ELS, Linthurst et al., 1986; Kanciruk et al., 1986). The ELS was conducted as a stratified random sample of lakes in 5 subregions of the Northeast, and allows quantitative extrapolation of lake data to defined target populations in the region. The ELS target population includes all lakes identified on 1:250,000 topographic maps (nominal minimum lake area of ca 4 ha, although the population of lakes smaller than 8 ha is underrepresented), and includes both natural lakes and impoundments. A total of 768 lakes were sampled in 1984 during fall overturn (Figure 4), representing a target population of 7096 lakes in the region.

For 145 of the ELS lakes, hydrologic inputs and outputs, deposition, and watershed soils, vegetation, and geology were characterized as part of the EPA's Direct/Delayed Response Project (DDRP) (Church et al., 1989). Dynamic model simulations, using the MAGIC model (Cosby et al., 1985a; 1985b) were subsequently conducted for 129 of these lake systems (seepage lakes and sites with significant watershed sources of sulfate were deleted from model simulations) as part of EPA/NAPAP analyses to project the number of lake systems likely to become acidic or to recover under a variety of sulfate deposition scenarios (Church et al., 1989; NAPAP, 1991). The maximum ANC of lakes used in the DDRP was 400  $\mu\text{eq/L}$ , so the distributions of ANC, base cations, and of related variables including critical load estimates, for ELS lake populations, while similar for lakes with ANC < 400  $\mu\text{eq/L}$ , are not directly comparable to those for DDRP lakes. It should also be noted that the DDRP data collection and analyses, including lake selection, sampling design, and aggregation procedures for soil chemistry data for watersheds, was designed for regional assessment purposes and was not optimized for a site-by-site analyses of the type presented here.

### **3.5 Precipitation and Runoff, Deposition**

Estimates of long-term average values of precipitation and deposition, developed for each watershed as the "Typical Year" deposition dataset in the DDRP (Church et al., 1989), were used for all estimates of sulfate critical loads. The development of deposition data is described in detail by Church et al. (1989); briefly the procedure involved use of 30 year average data for precipitation amount (National Climate Data Center), combined with deposition data for a representative year for a nearby precipitation chemistry (NADP/NTN) site. The selection of the nearby "reference" precipitation and wet deposition sites was comparable to a "nearest neighbor" procedure, except that protocols considered not only geographic proximity, but also elevation and terrain. Dry deposition was estimated for each watershed, based on estimates for 80 by 80 km grid points generated using the Regional Acid Deposition Model (RADM) (Chang et al., 1987), kriged to individual DDRP sites. Runoff estimates were developed as averages of 1951-80 runoff, and were generated from runoff contour maps developed for the DDRP by the US Geological Survey, with linear interpolation of contour estimates to individual DDRP watersheds (Krug et al., 1990).

### 3.6 Underlying Assumptions and Approximations

For all of the procedures used to estimate critical loads for this comparative analysis, it is important to recognize that several important approximations and simplifying assumptions were made:

1. Annual precipitation and runoff are assumed to be constant throughout the simulation period in dynamic model analyses.
2. The deposition and biological mobility of nitrogen is assumed to be constant at current levels in both steady state and dynamic model-based estimates.
3. Sulfate and base cations (including long-term dynamics related to sulfate adsorption, cation exchange and biological accretion) are assumed to be at steady state in the SSWC estimates, but adsorption and exchange are treated as dynamic variables in MAGIC simulations.
4. The only variable input besides sulfate is dry deposition of base cations, which was varied in MAGIC simulations according to a regression relationship (describing deposition of dry base cations as linearly and positively related to deposition of dry sulfate) developed during the DDRP (Church et al., 1989).

Along with the assumptions and approximations noted above, it is also important to recognize that important assumptions and simplifications are incorporated in the models used to estimate Critical Loads and to estimate F for the Steady State analyses. As examples:

1. As noted for the SSWC model in #3 of the preceding list, base cation exchange is assumed to be at steady state (i.e., there is no cation exchange contribution to neutralization of acidity). In addition, the SSWC model also implicitly assumes that the pre-acidification cation weathering rate has not changed with time or changes in soil acidity. Critical loads estimated using the SSWC model are in essence estimates of historic base cation weathering rates. They are as such, probably good estimators of critical loads under conditions in which the cation exchange buffer has been thoroughly depleted, but for most systems, they probably represent a conservative estimate of the current critical load for surface waters.
2. As pointed out by the developers of the SSWC model (Sverdrup et al., 1990), the validity of the empirical relationships embodied in equations used to define "F" is uncertain, particularly outside the systems for which those relationships were defined (i.e., lakes in the Adirondacks).

and Norway). Similarly, Equations 1 and 2 were used as defined in the draft Mapping Manual, despite uncertainties which are inherent in the estimation of  $F$ . For example, as  $F$  is defined in equations 3 and 4, or in equations 5 and 6, a fixed relationship is assumed to exist between the value of  $F$  and current surface water chemistry (i.e., the system is at steady state). One uncertainty in this analysis arises in the assumption that base cation relationships in the glaciated northeastern U.S. are comparable to those across across deposition gradients in Norwegian systems (i.e.,  $S = 400$ ).

Uncertainty in  $F$ , whether it results from the choice of algorithms used for estimation, or from the values used in those equations (e.g., choice of " $S$ " in equation 3), can substantially influence the resulting estimates of critical loads, and can result in unexpected apparent relationships. As an example, let us consider two lakes. Assume one lake is in an area where empirical data suggest an  $S$  of  $400 \mu\text{eq L}^{-1}$  be used to determine  $F$ ; the second lake is located in an area where the value of  $S$  should be more on the order of  $200 \mu\text{eq L}^{-1}$ . Both lakes have a current base cation concentration ( $BC_c$ ) of  $75 \mu\text{eq L}^{-1}$ . The calculated  $F$ 's for lakes #1 and #2 are then 0.29 and 0.56 respectively. This suggests that the mineral weathering rate in the watershed of lake #2 has a greater capacity to respond to increases in acidic deposition than does that of lake #1, and would consequently release more base cations to the system. Lake #2 should therefore have the higher of the two critical loads. Let us also assume that both systems have the same runoff rate ( $Q=1$ ), the same base cation deposition rate ( $BC_o=0$ ), and the same pristine and current sulfate deposition rates ( $SO_{4t}=70$ ;  $SO_{4o}=20$ ). If we choose an  $ANC_{\text{limit}}=0$  as our definition of a system receiving a critical load, Equation 2 reduces to  $CL = BC_o$ . However, when we calculate  $BC_o$  (and hence critical load) from Equation 1, we find that lake #1 is estimated to have the higher of the two pre-anthropogenic base cation concentrations (lake #1 =  $60.50 \mu\text{eq L}^{-1}$ ; lake #2 =  $47.00 \mu\text{eq L}^{-1}$ ), which is counter to the expectations based on the values of  $F$ .

Recognizing these assumptions and limitations, it is important to reiterate that the results presented in this report represent a demonstration only, and that none of the estimates presented here should be regarded as final or as "correct". Use of alternate models for computing critical loads, of alternate values of  $F$  or of other relevant watershed variables, or use of different simplifying estimates/assumptions, would be expected to result in estimates of critical loads that are different from those presented here. It is likewise important to recognize that selection of other receptors

(soils, vegetation), indicators, and/or other endpoints is similarly likely to result in different estimates of critical loads for sulfate.

### 3.7 Presentation of Results

In this demonstration study, critical load estimates were developed for all ELS lakes (steady state water chemistry approach) or for a subset (MAGIC) of the lakes as identified in Figure 4. For presentation purposes, data are summarized using the 0.5 by 1.0 degree (latitude/longitude) grids recommended by the UN-ECE mapping task force (UN-ECE, 1990). All grid maps presented here are shaded to represent the first percentile of the lake population within the grid; that is, shadings reflect the lowest estimated critical load within each grid. Data for the regional populations are also summarized using cumulative distributions and could similarly be summarized using cumulative distributions for individual grid squares.

In evaluating the data presented in the maps, it is important to recognize that some grids include data for several dozen lakes, others for only one or two lakes, and in the case of MAGIC projections, there are no lakes in some grids. These differences in sampling intensities have a significant effect upon final presentations of critical loads estimates in that, for grid cells including only a few sampled lakes, the computed critical load is likely not to reflect the lowest critical load of all lakes occurring within the grid. Examples of how sampling intensity can affect projections are depicted in Figures 5a and 5b. Figure 5a was produced by taking 1000 random sets of lake samples from the ELS population while varying the size of the sample set from 5 to 80% of the total population. Taking the Brakke-F sulfate critical loads from the whole population as a baseline, the frequencies at which the most sensitive lakes were detected at a given sampling intensity were plotted. This information shows, for example, that if 1000 field measurement surveys were conducted, each randomly sampling 5% of the ELS population in the northeast, a lake from the sensitive stratum in that population would be detected only 12% of the time. The sampling intensity effect can be further exhibited by comparing the Brakke-F sulfate critical loads predicted for the northeastern JOGG subregions using lakes sampled in the ELS versus DDRP populations (Figure 5b). In this case, the most sensitive lake from each population which was located within a subregion was used to define the critical load for that subregion. The result is that the same lake defined the critical load in only four out of fifteen subregions, even though the DDRP population was a non-

# BRAKKE-F SULFATE CRITICAL LOADS

## EFFECT OF SAMPLING INTENSITY

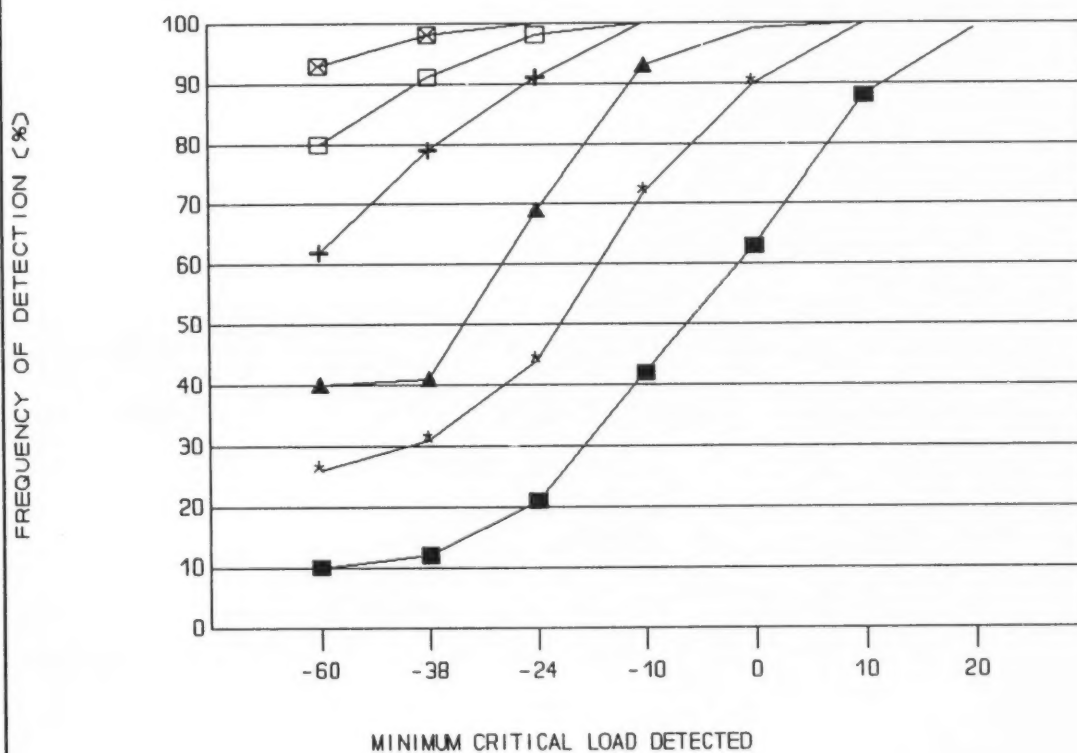


Figure 5a. Effect of sampling intensity on Brakke-F modeled sulfate critical loads. 1000 samplings taken from ELS population at 5, 10, 20, 40, 60, and 80% (■, \*, ▲, +, □, ⊠) intensities.

Lower sampling intensities lead to  
higher estimated Critical Loads

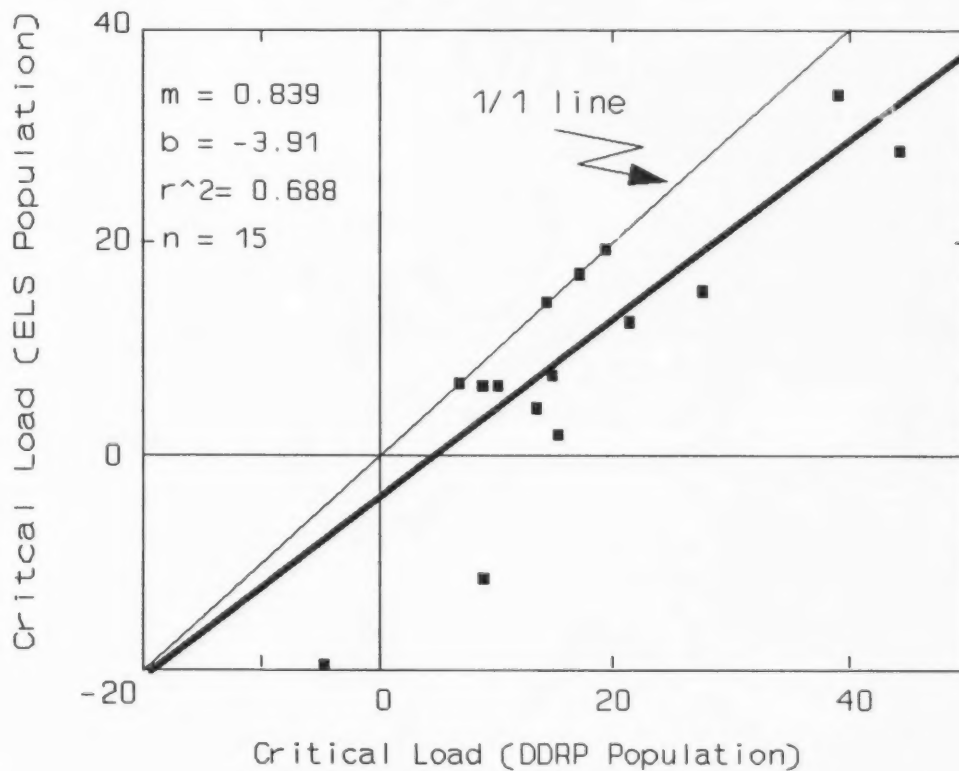


Figure 5b. Effect of sampling intensity on SSWC (Brakke-F) modeled critical loads. Data represent JOGG subregion critical load as determined by most sensitive lake from representative population.

random subsample which was specifically selected to represent the more sensitive end of the ELS population.

Similarly, spatial variability of the factors influencing critical loads of surface waters (e.g., lithology, soils) is unrelated to grid patterns, such that any individual grid might include a homogeneous population of surface water chemistries, or might conversely include several, heterogeneous types of lakes having a very wide range of critical loads. The U.S. mapping effort is currently evaluating the development of critical load maps delineated by factors such as bedrock geology, soils, etc. This demonstration study uses the simplest approach (grids) because it is recommended by the Task Force and because other approaches have firm theoretical bases, but require additional refinement. In addition, preliminary integrated analysis suggests that although regionalization schemes lead to very different critical loads maps and perceptions, they may not necessarily lead to different conclusions regarding emission control strategies.

## **4.0 RESULTS**

### **4.1 Comparison of Models and Sample Populations**

Distributions of computed critical loads are summarized and compared in Figures 6 and 7, as well as in Table 1. For the complete ELS population estimates of critical loads, based on the SSWC model, critical loads vary widely among watersheds, ranging from less than zero to more than 1100 kg SO<sub>4</sub>/ha/yr (Figure 6). For an ANC endpoint of 0 µeq/L, minimum estimates of critical loads are -37 and -31 kg SO<sub>4</sub>/ha/yr for Brakke-F and Paleo-F respectively, with corresponding median estimates of 51 and 44 kg/ha/yr. For an ANC endpoint of 0 µeq/L, 3 and 8 percent of lakes are estimated to have critical loads of < 0 kg SO<sub>4</sub>/ha/yr for Brakke-F and Paleo-F respectively, and 16 and 22 percent have estimated critical loads of less than 20 kg SO<sub>4</sub>/ha/yr. Critical load estimates based on Paleo-F values are consistently lower than those developed using Brakke-F, by roughly 10 kg SO<sub>4</sub>/ha/yr (Figures 6, 7, and Table 1).

In comparison to the SSWC estimates of critical loads, the distribution of critical loads estimates resulting from MAGIC simulations is substantially higher (Figures 6, 8 and Table 1). For an ANC endpoint of 0 µeq/L, none of the DDRP lakes are projected in MAGIC simulations to have critical loads less than zero, and only 1 percent of lakes have estimated critical loads below 20 kg

## CRITICAL LOADS FOR SULFATE

### COMPARISON OF APPROACHES

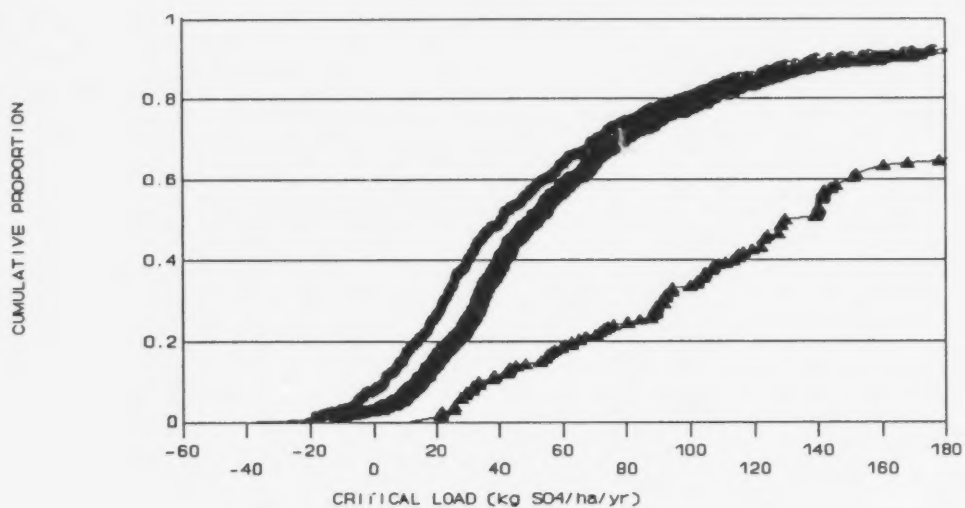


Figure 6. Cumulative distributions of sulfate critical loads for lakes in the ELS population of the northeastern U.S. (Brakke-F, —■—; Paleo-F, —\$—; MAGIC, —▲— [122 DDRP lakes only]).

Table 1. Summary distribution of estimated critical loads for sulfate in the Northeastern U.S., for all ELS lakes and for DDRP lakes only, for ANC endpoints of 0 and 25  $\mu\text{eq/L}$ , using three procedures for estimating critical loads. Units for critical loads are  $\text{kg SO}_4/\text{ha/yr}$ .

| n =                                                                                                   | Brakke - F |      |             | Paleo - F |     |     | Brakke - F |     |              | Paleo - F |    |     | MAGIC <sup>1</sup> |    |     |
|-------------------------------------------------------------------------------------------------------|------------|------|-------------|-----------|-----|-----|------------|-----|--------------|-----------|----|-----|--------------------|----|-----|
|                                                                                                       | 0          | 25   | 768         | 0         | 25  | 768 | 0          | 25  | 122          | 0         | 25 | 122 | 0                  | 25 | 122 |
|                                                                                                       |            |      | (ALL LAKES) |           |     |     |            |     | (DDRP LAKES) |           |    |     |                    |    |     |
| <u>Percentile of Distribution</u>                                                                     |            |      |             |           |     |     |            |     |              |           |    |     |                    |    |     |
| minimum                                                                                               | -37        | -43  | -31         | -36       | -14 | -20 | -22        | -27 | 12           | 1         |    |     |                    |    |     |
| 5                                                                                                     | 7          | -0   | -5          | -13       | 9   | 9   | -5         | -14 | 28           | 10        |    |     |                    |    |     |
| 25                                                                                                    | 30         | 23   | 19          | 12        | 19  | 11  | 7          | 1   | 84           | 56        |    |     |                    |    |     |
| median                                                                                                | 51         | 44   | 41          | 34        | 36  | 29  | 25         | 18  | 130          | 106       |    |     |                    |    |     |
| 75                                                                                                    | 91         | 84   | 83          | 76        | 64  | 58  | 55         | 46  | 202          | 178       |    |     |                    |    |     |
| 95                                                                                                    | 276        | 270  | 254         | 246       | 98  | 92  | 86         | 79  | 369          | 342       |    |     |                    |    |     |
| maximum                                                                                               | 1121       | 1114 | 1111        | 1104      | 112 | 105 | 106        | 99  | 632          | 597       |    |     |                    |    |     |
| <u>Percentage of population with estimated critical load less than (<math>\text{kg/ha/yr}</math>)</u> |            |      |             |           |     |     |            |     |              |           |    |     |                    |    |     |
| 0                                                                                                     | 3          | 5    | 8           | 13        | 2   | 4   | 9          | 22  | 0            | 0         |    |     |                    |    |     |
| 10                                                                                                    | 7          | 12   | 16          | 23        | 7   | 20  | 30         | 42  | 0            | 4         |    |     |                    |    |     |
| 20                                                                                                    | 16         | 22   | 26          | 37        | 28  | 38  | 45         | 52  | 1            | 13        |    |     |                    |    |     |
| 48                                                                                                    | 48         | 54   | 56          | 60        | 62  | 71  | 74         | 76  | 14           | 24        |    |     |                    |    |     |
| 96                                                                                                    | 77         | 79   | 79          | 82        | 95  | >99 | >99        | 100 | 34           | 48        |    |     |                    |    |     |

<sup>1</sup> 50 year simulation.

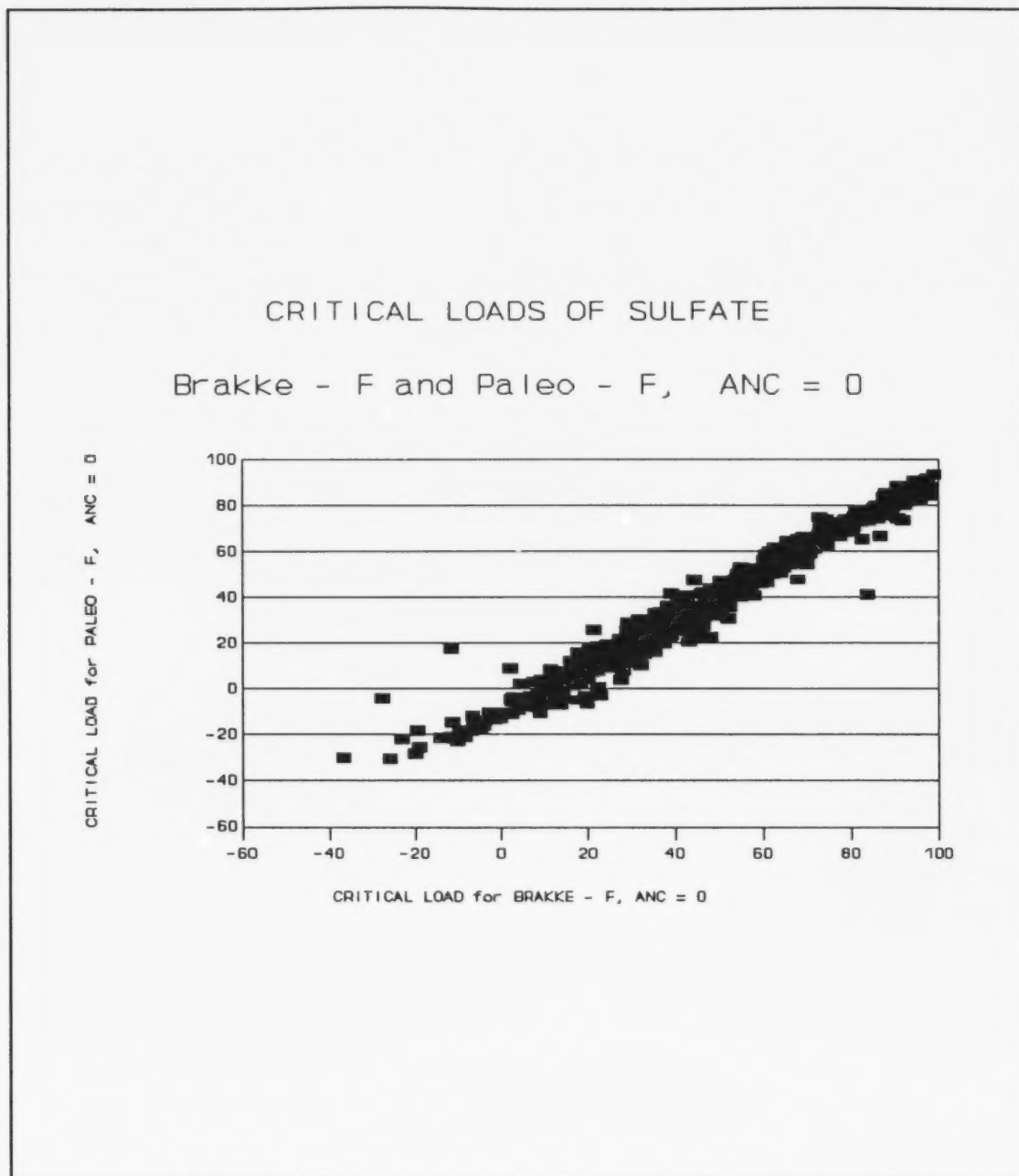


Figure 7. Comparison of Brakke-F and Paleo-F sulfate critical loads using ANC endpoint of 0  $\mu\text{eq/L}$ .

# CRITICAL LOADS OF SULFATE

Brakke - F and MAGIC (50 yr), ANC = 0

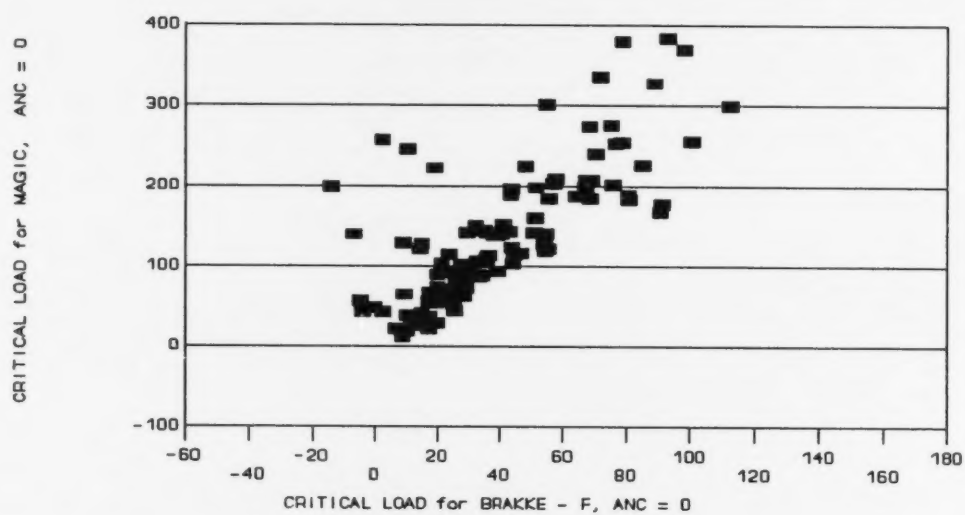


Figure 8. Comparison of Brakke-F and MAGIC sulfate critical loads using ANC endpoint of 0  $\mu\text{eq/L}$ .

SO<sub>4</sub>/ha/yr. Several factors contribute to the differences between MAGIC and Steady State-derived estimates of critical loads.

First, the approaches are fundamentally different, and incorporate different assumptions, approximations, and uncertainties, along with different time frames. Of particular note, the MAGIC projections are based on 50-year simulations, so cation exchange is presumably still influencing the estimates of critical loads (maintaining them at higher values than if MAGIC were run to steady state). Preliminary analysis of critical load estimates based on MAGIC simulations run to steady state suggests that the discrepancy between SSWC and MAGIC results is reduced, but is not eliminated (data not shown).

The differences in MAGIC and SSWC distributions cannot be explained by the different target populations used for the three sets of estimates. The DDRP population simulated by MAGIC includes only lakes with ANC  $\leq 400$   $\mu\text{eq/L}$ , with the result that lakes with high ANC and very high critical loads are not included in the MAGIC population. For the SSWC model, critical loads are thus shifted to lower values for the MAGIC population, widening the difference between SSWC and MAGIC estimates (Figure 9, Table 1). It should be noted that, for individual lake systems, the differences between SSWC and MAGIC estimates are minimized for low estimates of critical loads.

There are two principal explanations for the occurrence of lake systems with estimated critical loads of  $< 0$  kg SO<sub>4</sub>/ha/yr. Many of these values reflect systems that are naturally acidic, due principally to presence of organic acids; if deposition loads were reduced to background levels, these systems would be expected to remain acidic (although the relative concentrations of organic and inorganic anions would shift). In some cases, however, low estimates of critical loads can presumably also be attributed to imprecision in the estimation procedure, associated with values of F, and/or with historic sulfate concentrations used to calculate  $[\text{BC}]^*_0$ , with sea salt corrections, etc. For lakes in the Adirondack Mountains of New York, lakes identified as naturally acidic, based on diatom reconstructions, were excluded from the sample population and the distribution of critical loads was redefined. The resulting distribution (not shown) included fewer lakes with negative critical loads but was otherwise little changed.

## 4.2 Comparison of ANC Endpoints

For all three sets of critical load estimates, the estimated critical loads for an ANC endpoint of 25  $\mu\text{eq/L}$  are lower than those for  $\text{ANC} = 0$ . In the cases of the SSWC estimates, the differences are essentially linear shifts in critical load by ca 7 kg  $\text{SO}_4/\text{ha/yr}$  (Figure 10, Table 1), and follow directly from the value of  $\text{ANC}_{\text{limit}}$  used in the algorithm (Eqn. 2) used to estimate critical loads. The estimated percentages of lakes with critical loads less than zero (or any other specific value) also increased (e.g., from 3 to 5 percent for Brakke-F, 8 to 13 percent for Paleo-F) (Table 1). The difference in critical loads for MAGIC is somewhat larger than for SSWC estimates, and increases with the critical load. The lower critical loads for the 25  $\mu\text{eq/L}$  ANC endpoint, compared with those for an ANC endpoint of 0  $\mu\text{eq/L}$ , are consistent with theory, and are attributable to the fact that less acidification is required to reduce ANC from some initial value to  $\text{ANC} = 25$  than to reduce ANC to zero. The increase in the number of systems with critical loads of  $< 0$ , at an ANC endpoint of 25 compared to  $\text{ANC} = 0$ , in principle reflects those systems which historically, under "pristine" conditions, had  $\text{ANC} < 25 \mu\text{eq/L}$ , and therefore would require net additions of alkalinity to raise lake ANC to 25  $\mu\text{eq/L}$ .

## 4.3 Mapped Presentation of Critical Load Estimates

For critical loads estimated using the SSWC model with Brakke-F values and an ANC endpoint of 0  $\mu\text{eq/L}$  as a "base case" for comparative purposes, point maps and grid maps (0.5 x 1.0 degree, latitude/longitude) are shown in Figure 11. Low estimated critical loads (sensitive areas) are indicated by dark shading, high estimates by light shades. The gross spatial distribution of low critical loads in these figures is consistent with observed patterns of surface water ANC within the region. Systems having low critical loads are concentrated in the Adirondack Mountains of New York, the Pocono/Catskill Mountains of Pennsylvania and New York, and in southeastern New England (Rhode Island, eastern Massachusetts, and southern New Hampshire). Conversely, areas with high estimated critical loads coincide with areas lacking low ANC surface waters, such as the St. Lawrence/Champlain valley and northern Maine. Shading in the grid maps reflects the first percentile of critical load estimates within the grid; that is, each grid is shaded to reflect the lowest critical load estimated for a lake located within the grid. In some cases, shading is representative of numerous lakes within a grid estimated to have low critical loads (e.g., Cape Cod),

CRITICAL LOADS FOR SULFATE  
COMPARISON OF LAKE POPULATIONS

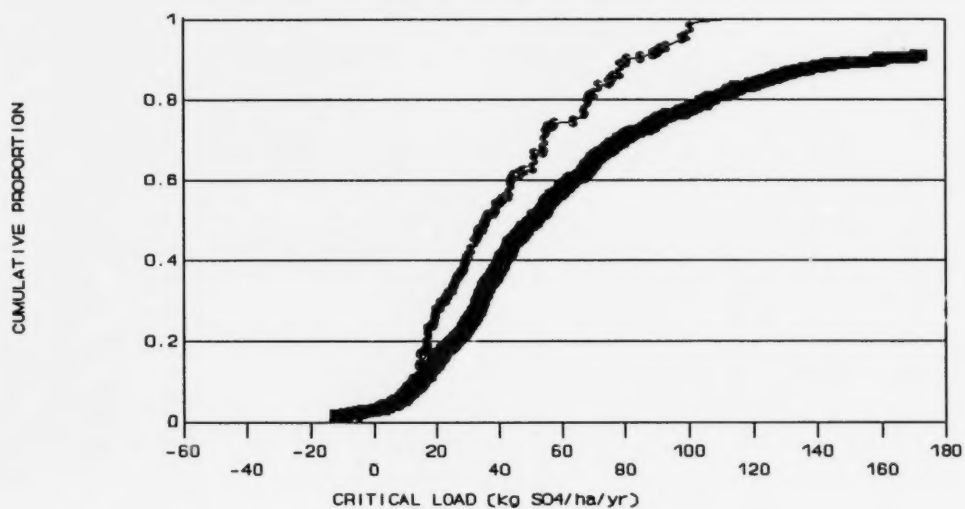


Figure 9. Comparison of cumulative distributions of Brakke-F sulfate critical loads for lakes in the ELS (—■—) and DDRP (—♦—) populations.

### CRITICAL LOADS OF SULFATE

Brakke - F, ANC = 0 and ANC = 25

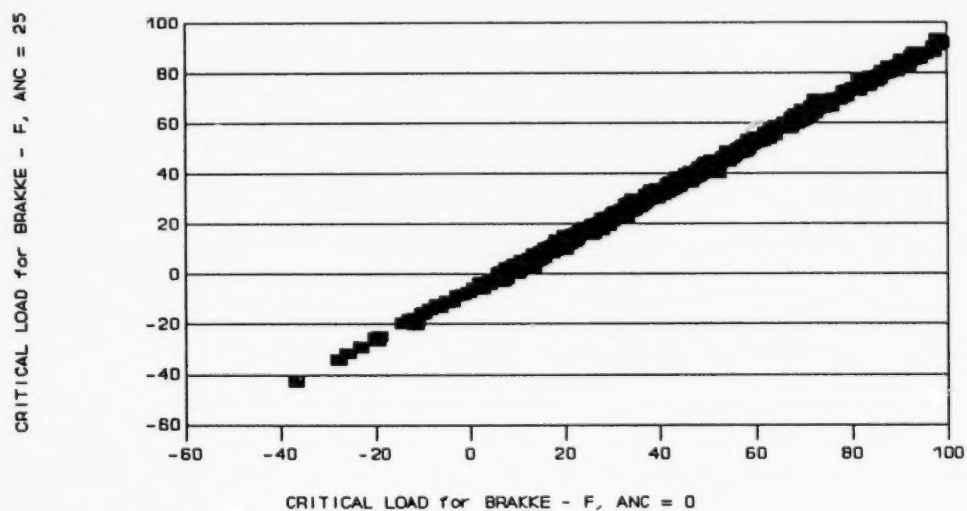


Figure 10. Comparison of sulfate critical loads for ANC endpoints of 0 and 25  $\mu\text{eq/L}$ . Estimated using Brakke-F.

Figure 11. Estimated critical loads of sulfate for lakes in the northeastern U.S., using Brakke-F values and for an ANC endpoint of 0  $\mu\text{eq/L}$ , showing results for individual lakes (a) and for data summarized to 1.0 by 0.5 degree grids (b)

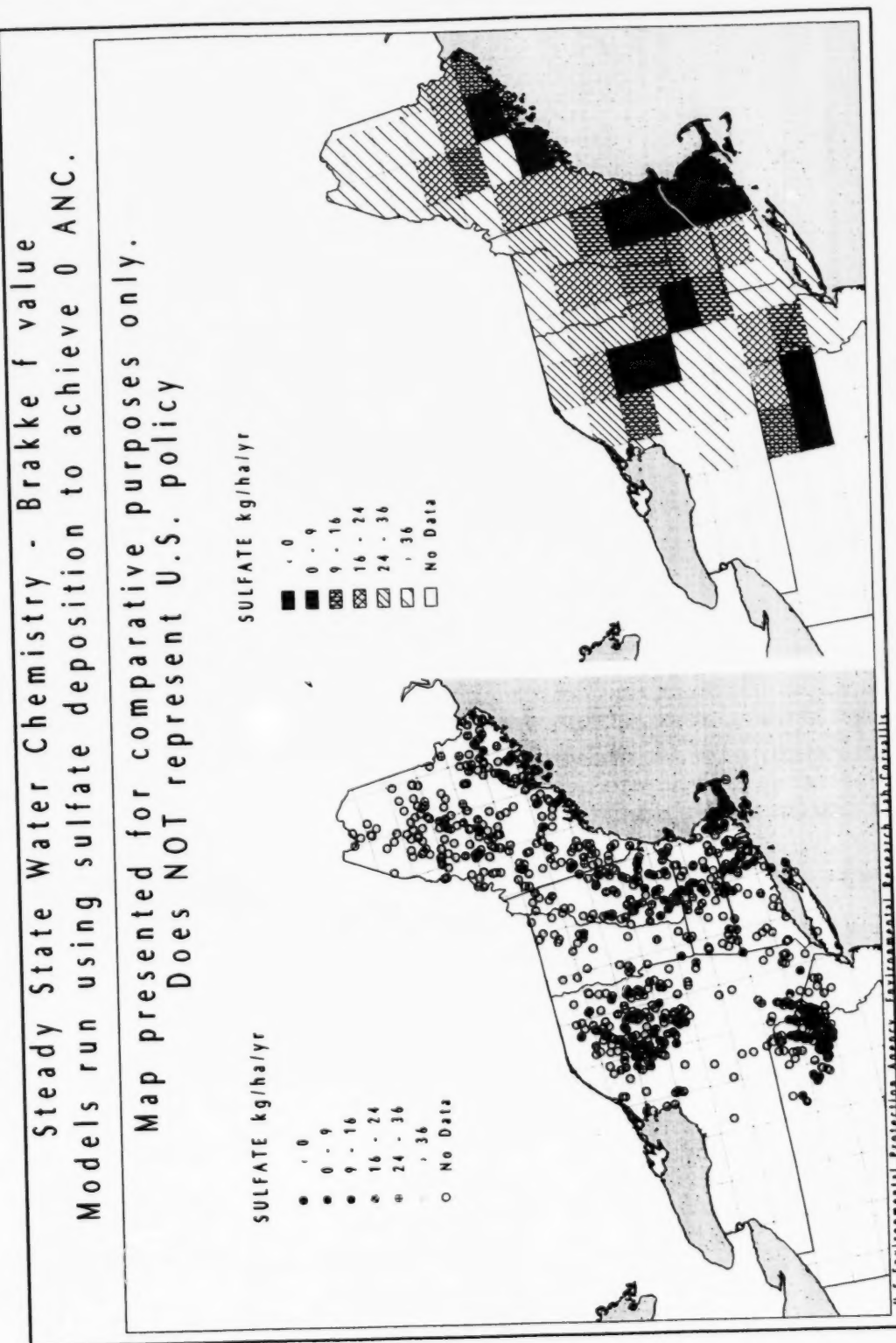


Figure 11a.

Figure 11b.

but in other cases shading can reflect a single lake in an area otherwise dominated by systems having high critical loads. At least one lake having a critical load of  $< 0$  occurs in about ten percent of the grid squares, and over half of the grids include lakes with estimated critical loads of 24 kg  $\text{SO}_4/\text{ha}/\text{yr}$  (500 eq  $\text{SO}_4/\text{ha}/\text{yr}$ ).

The spatial pattern of critical loads for  $\text{ANC} = 25 \mu\text{eq}/\text{L}$ , using SSWC with Brakke-F values (Figure 12), is very similar to that for  $\text{ANC} = 0$ , except, as noted above, that estimated critical loads are lower. The consistent offset of values, as shown in Figure 10, results from the algorithm used to compute critical loads (Eqn.2). Because of the lower estimated critical loads at the ANC endpoint of  $25 \mu\text{eq}/\text{L}$ , the shading of numerous grids has shifted to reflect lower critical loads (e.g., the fraction of grids including at least one lake with  $\text{CL} < 0$  has more than doubled).

The spatial distribution of Paleo-F critical loads (Figure 13a) has patterns of "high" and "low" critical loads that are comparable to those for Brakke-F, but the shift to lower estimates of critical loads results in a much higher frequency of grids with critical loads  $< 0$  and of other low reference values. The observed relationship between estimated critical loads for Brakke-F and Paleo-F was unexpected and appears to be counterintuitive. In general, for any given system, higher values of  $F$  imply more effective buffering, and should be reflected in higher estimates of critical loads. In this case, computed values of Paleo-F (Eq. 5,6) are consistently higher than those calculated for Brakke-F (Eq. 3,4), yet the resulting estimates of critical loads based on Paleo-F values are consistently lower. The observed relationship is apparently a direct and inevitable consequence of the two equations (Eq. 1 and 2) used to estimate critical loads in the SSWC model. In Equation 1,  $[\text{BC}]^*_0$ , for any given values of  $[\text{BC}]^*_t$  and  $\Delta\text{SO}_4$ , will vary negatively with  $F$  (i.e., the higher the value of  $F$ , the lower the resulting value of  $[\text{BC}]^*_0$ ). Computed values of critical loads from

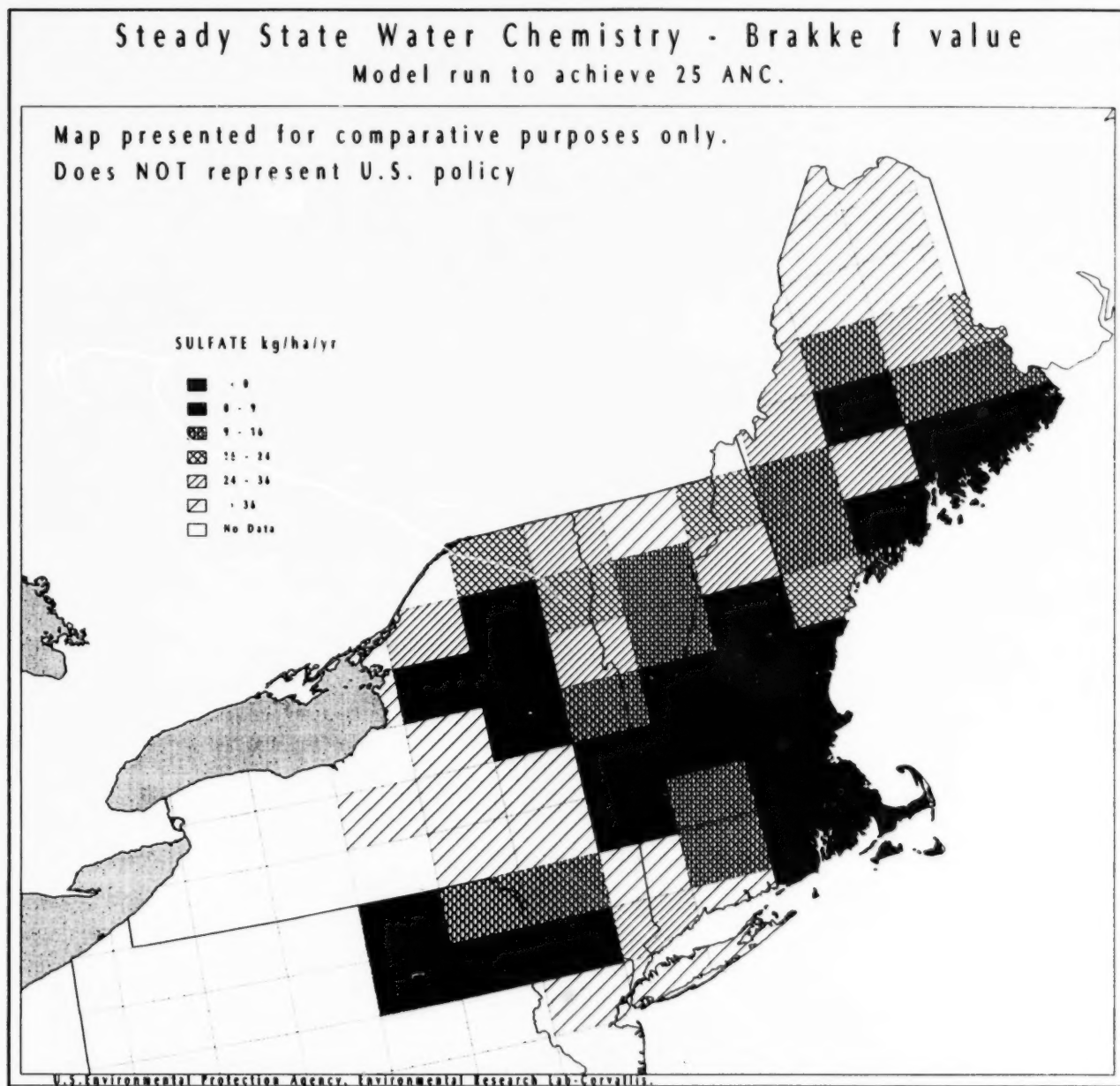


Figure 12. Estimated critical loads of sulfate for lakes in the northeastern U. S., computed using Brakke-F values at an ANC endpoint of 25  $\mu\text{eq/L}$ .

Figure 13. Grid maps for estimated critical loads of sulfate, for an ANC endpoint of 0 ueq/L, for all ELS lakes, using Paleo-F values (a), and for MAGIC-based estimates for DDRP lakes (b)

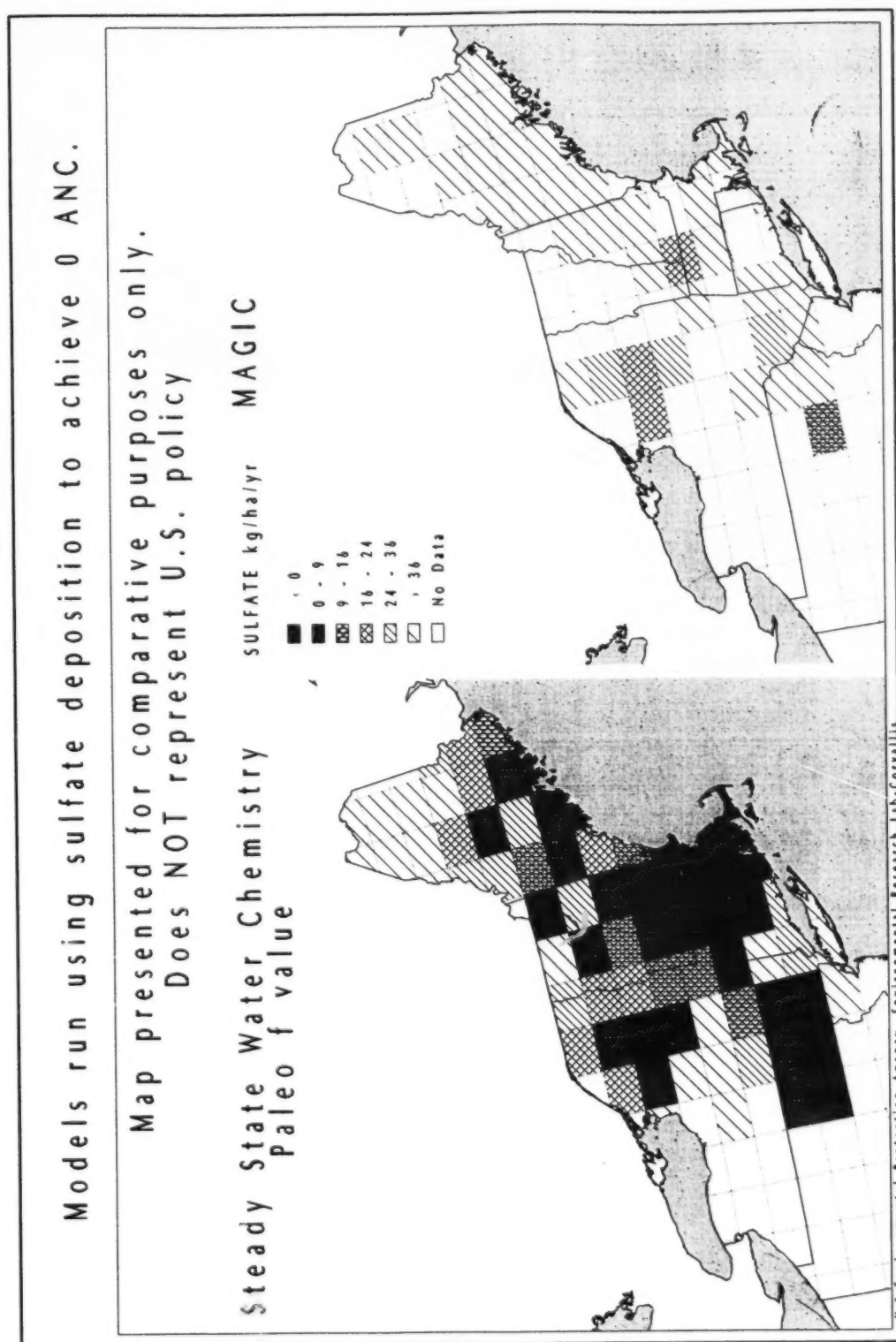


Figure 13a.

Figure 13b.

Equation 2 are directly related to  $[BC]^*_0$ ; that is the negative relationship between  $F$  and  $[BC]^*_0$  leads in turn to an equivalent negative relationship between  $F$  and the estimated critical load.

The mapped distribution of critical loads developed from MAGIC estimates (Figure 13b) differs in several respects from the SSWC (Brakke-F and Paleo-F) maps. Most apparent is the fact that because MAGIC simulations were run for a much smaller set of watersheds than the SSWC estimates, many of the grids did not contain any MAGIC lakes and in virtually all cases MAGIC grids included fewer lakes than the SSWC grids. The differences in critical load estimates are also obvious, as none of the grids include lakes with estimated critical loads  $< 0$ , and fewer than 25 percent of the grids include lakes with estimated critical loads lower than 24 kg  $SO_4$ /ha/yr. The spatial pattern of MAGIC-based critical load distributions is also somewhat different from Brakke-F and Paleo-F based distributions of critical loads and from observed distributions of surface water ANC. Low critical loads occur in the Adirondack and Pocono/Catskill areas, but not in southeastern New England. As discussed in Section 3.7, the smaller number of lakes in each grid in the MAGIC maps reduces the likelihood of including the lake with the lowest critical load in MAGIC-based critical load estimate for the grid (this factor is independent of the differences in the cumulative distributions of critical loads for the various populations).

## 5.0 DISCUSSION

This demonstration study has generated and compared results of three procedures for estimating critical loads of sulfate for surface waters in the northeastern United States. The three approaches result in often similar spatial patterns of relatively high and low critical loads, which are roughly comparable to patterns of high and low surface water ANC, but for any given lake system the three estimates generate significantly different critical load estimates. These differences highlight the uncertainties in estimating critical loads for surface waters, and reflect uncertainties in the information and procedures required to make those estimates (e.g., uncertainty in determining "true" values of  $F$ , uncertainty regarding the relative roles of cation exchange and mineral weathering in soil buffering, uncertainty in estimates of historic deposition (and of contemporary dry deposition) of sulfate and base cations).

The relationship between Brakke-F and Paleo-F estimates of critical loads emphasizes the importance of comparative studies to assess variability and uncertainty in model estimates, and

points out the need to carefully consider the assumptions and implications associated with the algorithms used to estimate critical loads. As described in Section 3.6, the coupled use of Equations 1 and 2 suggests a negative relationship between two variables which should be positively related,  $F$  and critical loads. Equation 1 describes historic changes in lake chemistry using one relationship for sulfate-base cation dynamics (described by  $F$ ), whereas the prediction of critical loads in Equation 2 is based on the difference between  $[BC]^*_0$  and  $ANC_{limit}$ , and implicitly sets  $F$  to 0. As a result, use of these equations give a result that higher  $F$ -values result in lower critical loads. If  $F$  were actually equal to zero, this equation would be correct, but actual values of  $F$  are greater than 0 in most systems and suggest a need to modify these equations.

The relationship between MAGIC and SSWC (using Paleo- $F$  values) estimates of critical loads is also inconsistent with a direct comparison of paleo reconstructions and MAGIC hindcasts for lakes in the Adirondack Mountains (Sullivan et al., 1991). That study showed that MAGIC-based estimates of historical acidification are greater than paleo estimates, implying that critical load estimates associated with MAGIC should also be lower than for paleo estimates.

Given the variability among estimates of critical loads, and our inability to verify any single set of estimates, it appears unwise at the present time, to adopt any of these single approaches for estimating critical loads. Pending continued careful review of procedures used to estimate critical loads, interim results should be appropriately caveated and should not be used as the basis for any policy considerations.

The uncertainties reflected in this demonstration project for sulfate become even more problematic in attempts to estimate critical loads for nitrogen. The complex biogeochemical cycling of nitrogen, combined with its importance as a macronutrient, greatly complicate any effort to describe and predict the future dynamics of, and ultimately the critical load for, nitrogen. As an example, Pardo (1991) has recently estimated critical loads for nitrogen at the Hubbard Brook Experimental Forest, New Hampshire, using several empirical models and data for several time intervals. The resulting estimates of critical loads ranged from 0 - 1700 mol N/ha/yr, compared to current deposition of approximately 500 mol N/ha/yr. The inability to constrain critical load estimates for nitrogen, even for a very data-rich site such as Hubbard Brook, suggests that a considerable amount of research and very extensive regional databases will be required before attempting to develop any meaningful regional estimates of critical loads for nitrogen.

Although there are substantial differences in the estimates of critical loads developed using the three procedures described in this study, it is also important to recognize consistencies in the various results:

1. All methods of estimation identify spatially-extensive areas of low critical loads for sulfate within the region.
2. The spatial patterns of high and low critical loads are generally similar among procedures, and are consistent with spatial patterns of surface water ANC within the region.
3. Estimated critical loads for an ANC endpoint of 25  $\mu\text{eq/L}$  are lower than for  $\text{ANC} = 0$ . This result is consistent with expectations regarding computation of critical loads, but is important in demonstrating that computed estimates of critical loads are not absolute, but are rather dependent on the selection of an indicator and endpoint;
4. For the two steady state sets of estimates, numerous systems are estimated to have critical loads of less than zero. Although some of these estimates are presumably the result of imprecision in estimates of the variables used to compute critical loads (sea-salt correction, values of  $F$ , etc.), others reflect the occurrence of naturally acidic surface waters (due principally to organic acids) or, for estimates using  $\text{ANC} = 25$ , the occurrence of systems with historic ANC between 0 and 25.

It is also important to note that the estimates reported here reflect critical loads relative to chronic surface water acidification using index values of lake chemistry and assuming annual average precipitation, runoff, and deposition. Changes in sulfate deposition to levels less than the computed critical loads based on these calculations, would in principle protect surface waters against chronic acidification if watersheds conditions were otherwise unchanged, but would not be adequate to prevent episodic acidification (unless an appropriately high ANC endpoint were selected), and might not be adequate if hydrologic regimes were altered, if biological demands increased for base cations and/or decreased for nitrogen, etc.

The spatial patterns of estimated critical loads and the sizes of grid cells, relative to regional airsheds in the eastern U.S. should also be noted. All of the results presented here have identified areas of relatively low critical loads in the western portion of the study area, in the portion of the region closest to major sulfur emission sources in the Ohio River valley and the midwestern U.S. If any of these preliminary results are confirmed by subsequent analyses, they suggest the need to

substantially reduce sulfur emissions in the source regions in order to reduce sulfate deposition in the Adirondack and the Pocono/Catskill regions, if sensitive aquatic resources in these regions are to be protected from (or restored from current) adverse effects of acidic deposition.

In closing, it is important to note that we have not attempted to evaluate or identify any of the results presented here as right/wrong or to rank the reliability of results. Our objective, rather, has been to generate sets of critical load estimates using multiple models and data sets, and to compare the results. The results presented here represent a first step in the critical evaluation of models used to estimate critical loads and to cross-validate model-based estimates. Our results have demonstrated substantial variability in critical loads estimated using different datasets and procedures. Given these results, it seems clear that extensive review, refinement, and verification of models and datasets will be required before any critical load estimates can be reliably used.

## 6.0 LITERATURE CITED

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